On the Specific Gravities of Niobium and Tantalum Pentoxides

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On the Specific Gravities

OF

Niobium and Tantalum Pentoxides

BY

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DISSERTATION

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PURPOSE

The original purpose of this investigation was to find a method for the determination of tantalum and niobium, without separation, based on the specific gravity of the combined oxides. Until recently,[1] the only available method for their determination was by fractional crystallization of the potassium double fluorides. In this method the mixed hydroxides of the elements are obtained by fusion with potassium bisulphate and boiling the melt with water. After removal of impurities and thorough washing, these hydroxides are dissolved in hydrofluoric acid, potassium fluoride added and the solution evaporated until the more insoluble tantalum salt separates. It is a difficult matter to free this salt from the mother liquor containing the niobium without, at the same time, dissolving some of the tantalum salt. That the method is inaccurate and unreliable, is shown by Metzger and Taylor.[2]

Penfield and Ford,[3] in an article on Stibiotantalite, in which tantalum and niobium were determined by a method based on the specific gravity of the combined oxides, say "As there is no satisfactory method for separating tantalum from niobium, the attempt has been made to determine the proportions of the two oxides by taking the specific gravity of the mixed oxides as obtained from the analysis, and comparing the results with those of pure Ta_2O_5 and Nb_2O_5, which are quite widely separated. This method has been tested sufficiently to prove that it gives fairly satisfactory results. . . . The greatest variation of the determination of Nb_2O_5 from these curves is not over one per cent., which is well within the errors of analysis."

It was thought that if the specific gravities of the oxides were

[1]"A New Rapid Volumetric Method for the Determination of Niobium in the Presence of Tantalum," Metzger and Taylor, to be published soon.

[2]Loc. Cit.

[3]"Am. Jour. Science," 1906, p. 72.

accurately determined under conditions which gave constant results, a curve could be used which would give the percentage of each oxide in a mixture by its specific gravity. This would obviate the separation of the elements in the analysis and greatly shorten it. In order to do this and have the results accurate to within 0.25 per cent., it was found that the specific gravity must be accurate to the third decimal. This meant even greater accuracy in the weights of the specific gravity flask and the liquid used. It was necessary that these weights should check within 0.0005 gm. This was one of the most difficult problems. The weights did not, as a rule, check within this limit, notwithstanding the fact that various forms of apparatus were employed.

While the work, primarily, had this object in view, it was found necessary later to change the purpose somewhat, and, therefore, the investigation has been divided into three parts.

Preparation and Properties of the Material

The niobium and tantalum oxides employed in this work were prepared from South Dakota columbite by fusion with potassium bisulphate, boiling with water, removing impurities as usual, leaving the mixed hydroxides of niobium and tantalum, which were then converted to oxides and separated as follows: The mixed oxides were treated in small portions by fusion with crystallized potassium bisulphate (the crystallized bisulphate is much more effective in decomposing the mixed oxides than is the fused pyrosulphate), sulphuric acid added to the melt to make it pasty, the mass poured into hot water, boiled and washed several times with hot water by decantation, the hydroxides transferred to a filter (using a hard rubber funnel) and the washing with boiling water continued until thoroughly washed. The hydroxides so obtained were dissolved through the filter paper with hydrofluoric acid. When about a liter of this hydrofluoric acid solution had been obtained, somewhat more than the required amount of potassium fluoride to form the double salt was added and the solution evaporated in a large silver dish until crystals of the tantalum double fluoride, K_2TaF_7, began to form on the surface. These crystals are long, fine needles. However, if the solution contains too much hydrofluoric acid, a niobium salt

separates in short prisms, not unlike the tantalum salt, but larger, and more insoluble than potassium niobium oxyfluoride, $K_2NbOF_5.H_2O$. The amount of acid present should be only sufficient to keep the tantalum salt in solution, *i. e.*, about 1 to 2 cc. per 100 cc. of solution.

As soon as crystals of tantalum began to form, the solution was allowed to cool slowly, the crystals filtered off, washed two or three times with cold water and allowed to drain. The solution was then further concentrated and a second crop of crystals obtained, which was kept separate from the first. On the third concentration, the solution was tested from time to time by taking out a drop or two of the liquid and allowing to cool to note the presence or absence of the niobium crystals. The niobium double fluoride crystallizes in lustrous plates easily distinguished from the tantalum salt. When the proper concentration had been reached, as shown by the above test, the solution was allowed to cool. The crystals obtained at this point, being a mixture of both salts, were rejected. The mother liquor from these mixed crystals was concentrated until two crops of the potassium niobium oxyfluoride were obtained. These two fractions of the niobium salt were kept separate. The mother liquor was rejected.

These operations were repeated until all the oxides were converted into the double fluorides and the mixed fluorides separated. All the "first crop" of tantalum salt was combined and recrystallized once. To the mother liquor from this the entire "second crop" of crystals was added and one crystallization made. The crystals from the last mother liquor were rejected. Finally, the two crops of crystals just obtained were united and recrystallized and the mother liquor rejected. This final lot of crystals constituted the material used in the subsequent work on tantalum. For the $K_2NbOF_5.H_2O$ the same general method of purification was employed.

There seems to be considerable lack of agreement among investigators with regard to the specific gravities and properties of the oxides of niobium and tantalum, as may be seen in the following paragraphs.

Abegg[1] gives the properties of tantalum pentoxide as a tasteless and odorless white powder which suffers no chemical change on heating. By continued heating, it becomes crystalline. Ebelmen[2] obtained well-formed orthorhombic prisms by heating Ta_2O_5 in a muffle furnace with phosphorous salt, which were crystallographically investigated by Mallard[3] and by Nordenskjöld and Chydenius.[4]

The specific gravity varies according to the method or preparation and is especially influenced by the length of time and intensity of heating, as is shown in the following example from Rose:[5]

The specific gravity of the oxide was 7.109.

Heated 1 Hour at Moderate Heat.	4½ Hours.	9½ Hours.	15½ Hours.
7.274	7.383	7.529	7.536

And after a further heating of eleven hours at a high temperature, 7.914. On still further heating, it rose to 7.994. By heating strongly in a furnace, it sank to 7.652, because the Ta_2O_5 became amorphous. On fusion with potassium bisulphate and again heating the hyrdoxide, the specific gravity was 8.257.

The values, given in the literature, vary between 7.03 and 8.26.[6] It is to be remarked, however, that many of the old determinations are quite unreliable on account of the use of impure Ta_2O_5.

In all cases in which the decomposition of the tantalum compounds has been effected by the use of potassium bisulphate, the product contains sulphuric acid, which cannot be removed by washing. To get rid of this, the hydroxide must be heated with ammonium carbonate.

Niobium pentoxide can be obtained by heating $K_2NbOF_5.H_2O$ with sulphuric acid in a platinum crucible until all the hydro-

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[1] "Handbuch der Anorganischen Chemie," Vol. III, part III, p. 853.

[2] "Ann. Chim. Phys." (3), 33, 34.

[3] Compt. Rend., 105, 1260.

[4] "Oefvers af. k. Vet. Ak. Förh," 1860, 3; "Pogg. Ann.," 110, 642.

[5] "Pogg. Ann.," 74, 285.

[6] Rose, "Marignac, Ann. Chim. Phys." (4), 9, 249; Deville and Troost, "Compt. Rend.." 60, 1121.

fluoric acid is driven off, boiling the residue with water, washing and heating. The precipitate must be washed with ammonia before it is heated, to remove the sulphuric acid. Obtained in this manner, it usually contains traces of alkali.

The specific gravity of the oxide varies between 4.37 and 4.46 when prepared by means of potassium bisulphate, and between 4.51 and 4.53 when prepared by heating ammonium niobium oxyfluoride.[1] Strongly heated, the oxide becomes crystalline.

Apparatus Employed

A pycnometer of about 30 cc. capacity, with a thermometer ground in, was first tried, but it was found that the evaporation of the water from the ground glass joint gave such variable results that this form could not be used. Then, a specific gravity flask with a long neck, fine ground, 20 cc. capacity and provided with a cap ground in the same manner, was used. The bottle itself, but not the neck, was surrounded with a vaccuum jacket. This was to guard against changes in temperature in handling, etc. The object in having such a long neck was to insure a good, tight joint, so there would be the least possible difference in the volumes of the liquid in the flask in separate determinations, caused by slight differences in pressure exerted in inserting the stopper. The cap, ground in the same way, fitted over the stopper, was to prevent any evaporation from the surfaces, between the neck and the stopper or from the top of the capillary tube in the stopper. This combination was found somewhat too heavy and cumbersome, and a similar flask, having a capacity of 10 cc., was substituted later. This was used in most of the work with water, but when chloroform was used, the flask was essentially like that above, except that there was no vacuum jacket.

It was found extremely difficult to obtain weights that checked within the desired limits. The total variation in the weights is great, but those taken within short periods of time checked much better.

Method

The method used in the first part of the work is essentially as

[1] Marignac, "Ann. de Chim. et Phys." (4), 8, 19.

given below. Some changes were made from time to time to suit new conditions.

The flask was weighed filled with water, the water poured out and a weighed amount of oxide in fine powder introduced, the air removed as explained later, the flask filled and weighed again. The difference in weight between the flask with the oxide and with water only was subtracted from the amount of oxide, and the amount taken divided by this value, giving the specific gravity.

In preparing the flask for weighing, the stopper was inserted each time with as near as possible the same pressure. Then all superfluous moisture was removed, that from the top of the capillary tube removed last, and the cap put on. It was found that much better weights could be made if the flask were now dipped in cold water and carefully dried with a clean cloth. After standing ten minutes in the balance case, the weight was taken. The oxide must be in a fine powder to reduce to a minimum the possibility of included air. As a further precaution, after introducing the oxide the flask was only partially filled with water, shaken with a rotary motion and the filling completed. In completing the filling it was necessary to run the water in slowly in order to leave a clear portion above that which had been shaken up, otherwise some of the fine oxide held in suspension would be lost when the stopper was inserted.

The oxides were prepared from the double fluorides as follows: A portion of the double fluoride, corresponding roughly to 1.00 gram of the oxide, was heated in a platinum dish with sulphuric acid until all the hydrofluoric acid had been driven off and copious fumes of SO_3 evolved. After cooling, the solution was slowly, and with vigorous stirring, poured into about 700 cc. of hot water. This was then boiled, the water poured off through a filter after allowing the hydroxide to settle, boiled up with about the same quantity of water twice more, and then filtered. The hydroxide, while still moist, was placed in a large platinum crucible and gently heated until dry. After this, the heat was raised, the paper burned off and the resulting oxide pulverized in an agate mortar to approximately 80 mesh.

On trying to filter the oxides after a determination, it was

found that nearly all of the finer portions ran through the paper. This solution, if left undisturbed, would remain cloudy for several weeks. On account of the difficulty of filtering, not more than one value was obtained from each portion in the first part of the work. It is possible that some of this finer portion was rehydrated to some extent (?).

EXPERIMENTAL

Part I

In this part of the work the flask was filled with boiled distilled water at room temperature, temperatures being recorded by a thermometer, graduated to read to 0.2° C., and the usual precautions taken in weighing. It was found that the weight of the flask filled with water must be taken before each determination, since the variation in the temperature of the water from day to day caused such a variation in the weight that a constant value could not be used. In many cases the weights obtained on one day did not check with those obtained on the next, though the temperature was the same. The flask was handled as little as possible after taking the temperature in order to avoid any change.

A number of weighings was made to determine the error in filling and in inserting the stopper and are given here:

Temperature.	Weight.	
20.8	65.2000	a
20.8	65.1992	
20.8	65.1983	
20.8	65.1980	
20.8	65.2002	b
20.8	65.2002	
20.8	65.1987	
20.8	65.1978	
20.8	65.1972	

In a series of weighings the values varied in this manner, then, after a period of rest, as allowing to stand over night, the weight returned practically to the original value. Series (a) was obtained one day and series (b) on the following day. The variation was sometimes in one direction and sometimes in the other.

A number of determinations was made to ascertain if constant

results could be obtained by washing the hydroxide with water alone. It was thought that the sulphuric acid could be so far removed as not to cause appreciable error, even though it is practically impossible to remove all of it.

The table with the results is given and the detailed description of the conditions of each experiment follows:

No.	Weight Flask and Water.	Weight Flask and Oxide.	Weight Oxide.	Temperature.	Gravity.
1	65.1918	65.6066	0.5411	23.0	4.284
2	65.1945	65.8617	0.8659	22.2	4.357
3	65.2020	65.9425	0.9570	21.2	4.420
4	65.1893	66.1641	1.2661	23.2	4.344
5	65.2003	66.1697	1.2774	20.8	4.147
6	65.2026	66.2168	1.3258	20.4	4.254
7	65.1913	66.1797	1.2996	23.0	4.176
8	65.1978	66.1852	1.2847	21.4	4.322
9	65.1870	66.0078	1.0662	22.9	4.344
10	65.1834	66.0211	1.0738	23.7	4.459
11	65.1974	66.0128	1.0513	20.5	4.456

(1) About 1 gm. $K_2NbOF_5.H_2O$ was heated with sulphuric acid until fumes of SO_3 were given off, and the solution poured, with stirring, into 700 cc. hot water. This was boiled ten minutes, allowed to settle and boiled with fresh portions of water for the same length of time twice more. The hydroxide was filtered and dried. A moderate blast was then applied for thirty minutes.

(2) The same method of preparation was followed as in (1), except that the blast was used only twenty minutes.

(3) The blast was here applied forty minutes and the method of preparation the same as in (1).

(4) About 3 grams $K_2NbOF_5.H_2O$ were treated with 20 cc. sulphuric acid and the solution poured, with stirring, into two liters of hot water, boiled, and washed on the filter with one liter of boiling water. The hydroxide did not settle well. It was then dried, powdered and heated for one hour in a platinum crucible at a full red heat.

(5) The same amount of $K_2NbOF_5.H_2O$ was treated as in (4). 10 cc. sulphuric acid were used and the hydroxide washed with

two liters of hot water on the filter, after being boiled with one liter. The hydroxide settled well and washed easily.

(6) The same amount of $K_2NbOF_5.H_2O$ as in (4) was treated with 10 cc. sulphuric acid, poured into two liters of hot water, boiled, filtered and washed with three liters of hot water. Dried and heated one hour in a platinum crucible at a full red heat.

(7) Three grams $K_2NbOF_5.HO_2$ were treated with 12 cc. sulphuric acid, hydrolyzed in three liters of hot water, boiled, decanted and boiled with the same amount four times, then filtered and dried. A moderate blast was applied to the oxide for ten minutes.

(8) Three grams $K_2NbOF_5.H_2O$ treated in the same manner as (7).

(9) Two and a half grams $K_2NbOF_5.H_2O$ treated with 12 cc. sulphuric acid, hydrolyzed in two liters of hot water and boiled three times with the same amount. The filter paper was burned off at a low temperature and a higher blast used than in (7) and (8) for ten minutes.

(10) Two and a half $K_2NbOF_5.H_2O$ treated in the same manner as in (9).

(11) Two and a half grams of $K_2NbOF_5.H_2O$ treated in the same manner as in (9).

In the foregoing experiments the oxide increased in weight on standing on the balance pan. Notwithstanding the thorough washing of the hydroxide and the prolonged and intense heating it is interesting to note that the oxides, when ground in an agate mortar, were invariably slightly sticky and adhered to the mortar, due, undoubtedly, to the attraction of moisture by a small amount of sulphuric acid still present in the oxide, which opinion seems to be further borne out in the subsequent experiments.

Another series was made, using ammonium hydroxide to neutralize the sulphuric acid present.

No.	Weight Oxide.	Temperature.	Gravity.
12	1.0520	20.5	4.974
13	1.0772	20.6	4.936
14	1.0619	22.2	5.047
15	1.0635	21.5	4.914
16	1.0620	22.0	4.482

(12) Two and a half grams $K_2NbOF_5.H_2O$ were treated with 12 cc. sulphuric acid, poured into one liter of hot water, boiled and allowed to settle. Boiled twice more with one liter of water, the last portion being made slightly alkaline with ammonium hydroxide before filtering. The oxide was heated with a Chaddock burner until the paper was burned off, usually about forty-five minutes. The crucible was surrounded with a clay cylinder and the temperature regulated so that the bottom of the crucible was red.

(13) Same as (12).

(14) Two and a half grams $K_2NbOF_5.H_2O$ treated with 12 cc. sulphuric acid, poured into one liter of hot water and washed twice by decantation with the same amount of hot water, boiling each time. No ammonium hydroxide was used in the last wash water. The same low heat was applied until the paper was incinerated, the oxide ground and placed in a crucible with concentrated ammonium hydroxide and heated again for twenty minutes at a low red heat.

(15) Same as (14) except that the partially dried hydroxide was mixed with ammonium carbonate and heated in the usual manner.

(16) Same as (7) except that after filtering the hydroxide was washed on the filter with strong ammonia and on account of the gelatinous character, the precipitate probably did not receive a thorough treatment with the alkali.

In these experiments the oxide did not gain in weight, except that of (16), which apparently still contained some sulphuric acid. In the following work the last portion of water used in washing the hydroxide was always made distinctly alkaline before filtering.

In the following determinations about 2.5 grams $K_2NbOF_5.H_2O$ were treated with 12 cc. sulphuric acid, poured into one liter of hot water, boiled, washed twice by boiling and decantation, the last wash water made alkaline with ammonium hydroxide. The hydroxide, after drying at a low temperature, was heated for one hour at a low red heat.

No.	Weight Oxide.	Temperature.	Gravity.
17	1.0870	22.7	4.954
18	1.0221	20.6	4.973
19	1.0163	21.6	4.936
20	1.1354	23.3	4.932
21	1.1461	23.5	4.950
22	1.1051	25.3	4.962
23	1.1097	24.55	4.960
24	1.1133	24.8	4.952

The average of these determinations is 4.949, which represents the value of the specific gravity of Nb_2O_5 under these conditions.

For the corresponding value of the tantalum oxide the same conditions were used in the preparation of the oxide, ignition, etc., as in the case of the niobium oxide.

No.	Weight Oxide.	Temperature.	Gravity.
25	1.1745	22.9	7.909
26	1.1883	23.3	7.909
27	1.1600	23.4	7.854
28	1.2207	22.9	7.916
29	1.1910	23.7	7.856
30	1.2060	23.6	7.805
31	1.1543	22.7	7.857

These results give an average of 7.872 as the specific gravity of Ta_2O_5 under these conditions. On account of the smaller displacement, the variation is greater in these determinations than that in the case of niobium.

Knowing that difference in the length of time and intensity of the heat applied makes a difference in the specific gravity, it was decided to make a series of determinations, using a higher temperature for the same length of time as above. The preparation of the sample was the same as before, but the oxide was heated with the full flame of the Chaddock burner for one hour. This gave a bright orange heat.

No.	Weight Oxide.	Temperature.	Gravity.
32	1.1573	22.2	8.362
33	1.1588	21.9	8.277
34	1.1574	22.1	8.362

No.	Weight Oxide.	Temperature.	Gravity.
35	1.1485	22.3	8.310
36	1.1512	22.4	8.294
37	1.1592	22.5	8.303
38	1.1263	21.9	8.373
39	1.1604	22.0	8.371
40	1.1718	21.8	8.281
41	1.1754	21.9	8.353

This gives an average of 8.328 as the specific gravity of Ta_2O_5 at a higher temperature.

An exactly similar series was made on niobium pentoxide to find the value under the above conditions.

No.	Weight Oxide.	Temperature.	Gravity.
42	1.1209	23.2	4.844
43	1.0951	23.1	4.849
44	1.0778	23.0	4.807
45	1.1094	23.8	4.802
46	1.0865	24.2	4.835
47	1.0867	23.2	4.806
48	1.1215	23.4	4.852

These results give an average of 4.828.

This would seem to indicate that with increasing heat the specific gravity of the tantalum oxide increases, whereas that of the niobium oxide decreases. It was thought possible that there might be slight differences in the hydrolysis in the separate experiments above, which would affect the results, therefore, two larger portions of about double the quantity of salt were taken and treated as usual. After the hydroxides had been obtained, each of these was divided into two parts. Each pair of hydroxides was ignited separately under the same conditions, *i. e.,* the first pair at a full red heat for one and a half hours, the second pair at the same temperature for two and a half hours.

No.	Weight Oxide.	Temperature.	Gravity.
49	1.1017	23.6	4.702
Second half	1.1134	23.6	4.770
50	1.1713	22.9	4.370
Second half	1.1505	22.9	4.329

Each pair shows no greater disagreement than obtains where the portions were prepared separately. The length of time of heating, however, has a marked influence on the values.

Mixtures

Using the average values obtained for tantalum and niobium at a full red heat, 8.328 and 4.828, a curve was plotted and mixtures made to determine whether the per cent. of tantalum and niobium could be obtained in this manner.

The pure oxides, or mixtures of the same, are usually very slightly grayish in color when prepared by fusing the oxides with potassium bisulphate, hydrolyzing, etc., but those prepared from the double fluorides are white. This was thought due to the presence of a slight amount of platinum. An effort was made to make them whiter by dissolving the hydroxides in hydrofluoric acid, filtering, taking down to fumes again with sulphuric acid and rehydrolyzing, but the result was the same. The color is nearly always the same, and if there is any error due to this, it would be constant.

In preparing the mixtures, weighed amounts of the oxides were fused with potassium bisulphate, sulphuric acid added to make the melt more fluid, hydrolyzed and washed by decantation through a filter, etc., as already described. After drying, the hydroxides were heated for one hour at the full temperature of the Chaddock burner, pulverized, weighed and the specific gravity taken.

The mixture had the following proportions: Nb_2O_5, 0.5897 gm., and Ta_2O_5, 0.6899 gm., corresponding to 46.08 per cent. Nb_2O_5 and 53.92 per cent. Ta_2O_5. The specific gravity was 6.345, which, according to the curve, gave 56.50 per cent. Ta_2O_5, an error of 2.58 per cent.[1]

Part II

On account of many difficulties encountered when water was used as the liquid in which the specific gravity was taken, some other liquid was sought. The purpose of heating of the oxides is to dehydrate the hydroxides, and on being immersed in water,

[1] The curve is not shown here for this single experiment.

it is probable that a second determination on the same sample would vary on account of differing degrees of rehydration. If some liquid were used which had no effect of this kind, and in which the finely powdered oxides settled readily and were easily filtered, this effect could be avoided and a number of determinations made upon the same portion, the period of heating in each determination being simply a continuation of the preceding and the effect cumulative.

A number of such liquids were tried, including bromoform, benzol, xylol, chloroform, etc. Chloroform was finally selected, having a comparatively low boiling point and easily handled. On account of the low boiling point, the oxides were very easily dried. A number of methods were tried to obtain the most constant results. The co-efficient of expansion of chloroform being larger than that of water and its specific gravity greater, it was necessary to maintain as constant temperature conditions as possible.

One method used was to employ a large flask filled with chloroform at room temperature. From this the chloroform was forced by air pressure into the gravity flask, in order to avoid handling; a thermometer was kept in the chloroform at all times, but the variations in weight were too great for even as accurate work as in the case where water was used, and this method was discarded.

A second method was to use a constant temperature bath, as follows: A large, three-liter beaker served as the bath, being well protected by cloth and felt. A smaller beaker, of tall form, about 700 cc. capacity, was suspended in the center of the larger one by a wooden cover, provided with a hole of proper size. The smaller beaker was nearly filled with chloroform and the larger beaker filled with water. Before each determination, the gravity flask was immersed in the chloroform and the liquid agitated until the temperature was constant. The flask was filled and the stopper inserted while still in the chloroform vapor. It was found impossible to obtain concordant weights for the flask filled with chloroform in this way, and the method was abandoned.

A third method was decided upon and used throughout the

remainder of the work. To obtain a constant temperature a bath of boiling chloroform was used and the flask placed in its vapor. The chloroform was boiled in a Victor Meyer vapor density tube and the gravity flask suspended in a wire basket about an inch and a half above the boiling chloroform. A thermometer, graduated to hundredths of a degree C., was suspended in the tube to record temperatures. Platinum wire was used to insure uniform boiling and the heat was supplied by an electric hot plate.

No reflux condenser was needed, as the vapor was all condensed about three or four inches from the top of the tube The temperature of the vapor varied about 0.6° on different days (from 60.40° to 61.03°), depending upon the barometric pressure. This, however, did not affect the accuracy of the weights, since the two required for a determination were taken in comparatively short intervals of time, and the barometric change in that time was negligible.

A gravity flask with a long and well-fitted stopper, but without a vacuum jacket, was used. Determinations were made as follows: The flask filled with chloroform was heated for ten minutes in the bath, allowed to cool ten minutes and weighed, the cap being placed on the flask as soon as the small amount of chloroform on the outside had evaporated. This was practically accomplished by the time the flask had been removed from the tube. The flask was then emptied and a weighed amount of oxide introduced. It was partially filled with chloroform and again heated. This served to remove any air that might be included in the powdered oxide. The flask was then removed from the bath, shaken with a rotary motion, filled, and the stopper replaced, again suspended in the bath and the heating continued for ten minutes longer. The weight was taken after allowing to cool ten minutes.

It is important that the flask be only partially filled when suspended in the bath for the first time, for if completely filled, vapor invariably forms inside the flask, causing serious errors. It is equally important that the lower surface of the stopper be rounded and well polished. It is also required that the oxide be dried on the filter paper and then removed before reheating

for another determination. If the paper is incinerated with the oxide, vapor always forms in the flask when this oxide is again employed for a gravity determination.

The average of four weights of the flask filled with chloroform and an average of the same number of weights with the flask filled with water in the same bath was made. The weight of the flask alone being known, the ratio of chloroform to water at this temperature (60.80° C.) was found to be 1.432.

The material for the following experiments was prepared in a somewhat different manner from that of the first part. A large quantity of niobium double fluoride was treated in small lots until about 50 grams of the pure oxide was prepared. This was then placed in a large crucible and heated for one hour at a full red heat, avoiding thereby the probability of separate portions differing in specific gravity on account of slight but unavoidable differences in preparation.

A number of determinations was made on the oxide prepared as just described. It was thought at first that a weight could be determined upon by a series of weighings which would be constant for the flask filled with chloroform. But it was found that a separate weighing must be made for each determination, as before. This was due to the difference in barometric pressure on different days and the same gradual increase in weight of the flask for a time and after a period of rest, a return to nearly the original weight, as mentioned in the case where water was used (page 10).

No.	Weight Flask and $CHCl_3$.	Weight Flask and Oxide.	Weight Oxide.	Gravity Referred to $CHCl_3$.
51	30.2674	30.9878	1.0220	3.388
52	30.2692	30.9826	1.0127	3.383
53	30.2683	30.9818	1.0134	3.380
54	30.2683	30.9955	1.0330	3.375
55	30.2674	30.9792	1.0160	3.340
56	30.2684	30.9806	1.0176	3.340
57	30.2670	30.9757	1.0123	3.334

The last three results were made upon a different lot of oxide, prepared, however, as nearly as possible in the same manner. Another sample of oxide, prepared as nearly as possible as before, gave the following results:

No.	Weight Oxide.	Gravity Referred to $CHCl_3$.
58	1.0138	3.238
59	1.0192	3.248
60	1.0151	3.227
61	1.0400	3.224
62	1.0337	3.236
63	1.0349	3.244
64	1.5238	3.234
65	2.0475	3.224

These results show a maximum difference of 0.024, which was regarded sufficiently accurate for this work. The results on the three different samples (Nos. 51-54, 55-57 and 58-65) differing as they did, showed beyond question that the method of preparation and the length of time of heating the oxide were very important factors in obtaining a constant specific gravity.

This led to a series of determinations on one sample, heating a specified time before each determination, to find if any point could be reached where the gravity remained practically constant.

For this purpose a quantity of the niobium pentoxide was prepared in the usual way in small quantities and the entire lot thoroughly mixed and heated for one hour at a full red heat. From this lot the portions for the following experiments were taken. Each group represents the determinations on one sample until the gravity remained practically constant. The temperature employed for these ignitions was a full red heat.

No.	Weight Oxide.	Time of Heating.	Gravity Referred to $CHCl_3$.	
66	1.2230	20 mins.	3.186	
67	1.2008	20 " more.	3.178	
68	1.1956	25 " "	3.166	
69	1.1822	25 " "	3.152	A
70	1.1829	25 " "	3.158	A
71	1.2339	20 mins.	3.188	
72	1.2298	20 " more.	3.171	
73	1.2114	30 " "	3.166	
74	1.2055	25 " "	3.159	B
75	1.2026	20 " "	3.159	B

No.	Weight Oxide.	Time of Heating.	Gravity Referred to $CHCl_3$.	
76	1.2361	50 mins.	3.162	C
77	1.2415	20 " more.	3.159	C
78	1.2354	20 " "	3.161	C
79	1.2243	30 " "	3.156	C
80	1.2223	20 " "	3.160	C
81	1.2145	20 mins.	3.183	
82	1.2094	20 " more.	3.178	
83	1.1987	30 " "	3.159	D
84	1.1851	20 " "	3.162	D
85	1.1861	20 " "	3.159	D

In each of these groups the gravity gradually diminished until it became practically constant.

In the next experiments two portions of about three grams each of $K_2NbOF_5.H_2O$ were taken and the oxide prepared in the usual way. Determinations were made on these to see if the gravity would reach approximately the same value obtained above.

No.	Weight Oxide.	Time of Heating.	Gravity Referred to $CHCl_3$.	
86	1.2855	30 mins.	3.300	
87	1.2658	35 " more.	3.190	
88	1.2555	20 " "	3.161	E
89	1.2473	20 " "	3.159	E
90	1.2375	20 " "	3.159	E
91	0.9570	20 mins.	3.346	
92	0.9304	25 " more.	3.242	
93	0.9079	30 " "	3.174	
94	0.9175	30 " "	3.161	F
95	0.9141	20 " "	3.158	F

The final values obtained in the last two groups agree fairly well with those obtained above and were included in the general average. The results marked A, B, C, D, E and F were assumed to be constant and the average gave 3.159.

Later in the work the gravity of niobium was re-determined to see if the results obtained above could be duplicated under the same conditions. An average of three closely-agreeing values gave 3.161.

Tantalum Pentoxide

The method employed for the preparation of the tantalum pentoxide was the same as that described for the niobium pentoxide. Each of the groups shown below represents determinations on a separate portion of oxide taken from one stock supply.

No.	Weight Oxide.	Time of Heating.	Gravity Referred to $CHCl_3$.	
96	1.2236	40 mins.	6.191	
97	1.1985	20 “ more.	6.127	
98	1.1900	20 “ “	6.140	
99	1.1852	20 “ “	6.097	A
100	1.1775	20 “ “	6.084	
101	1.2010	40 mins.	6.062	
102	1.1943	20 “ more.	6.093	
103	1.1895	20 “ “	6.205	
104	1.2841	20 “ “	6.085	B
105	1.1760	20 “ “	6.090	
106	1.2117	20 mins.	6.098	
107	1.2001	20 “ more.	6.097	
108	1.1828	20 “ “	6.079	
109	1.1824	20 “ “	6.067	C
110	1.1680	20 “ “	6.055	
111	1.2158	40 mins.	6.018	
112	1.2004	20 “ more.	6.096	
113	1.1872	20 “ “	6.057	D
114	1.1789	20 “ “	6.077	
115	1.2201	40 mins.	6.061	E
116	1.2019	20 “ more.	6.070	
117	1.1855	20 “ “	6.061	
118	1.1784	20 “ “	6.074	
119	1.1766	20 “ “	6.087	
120	1.1644	20 “ “	6.064	

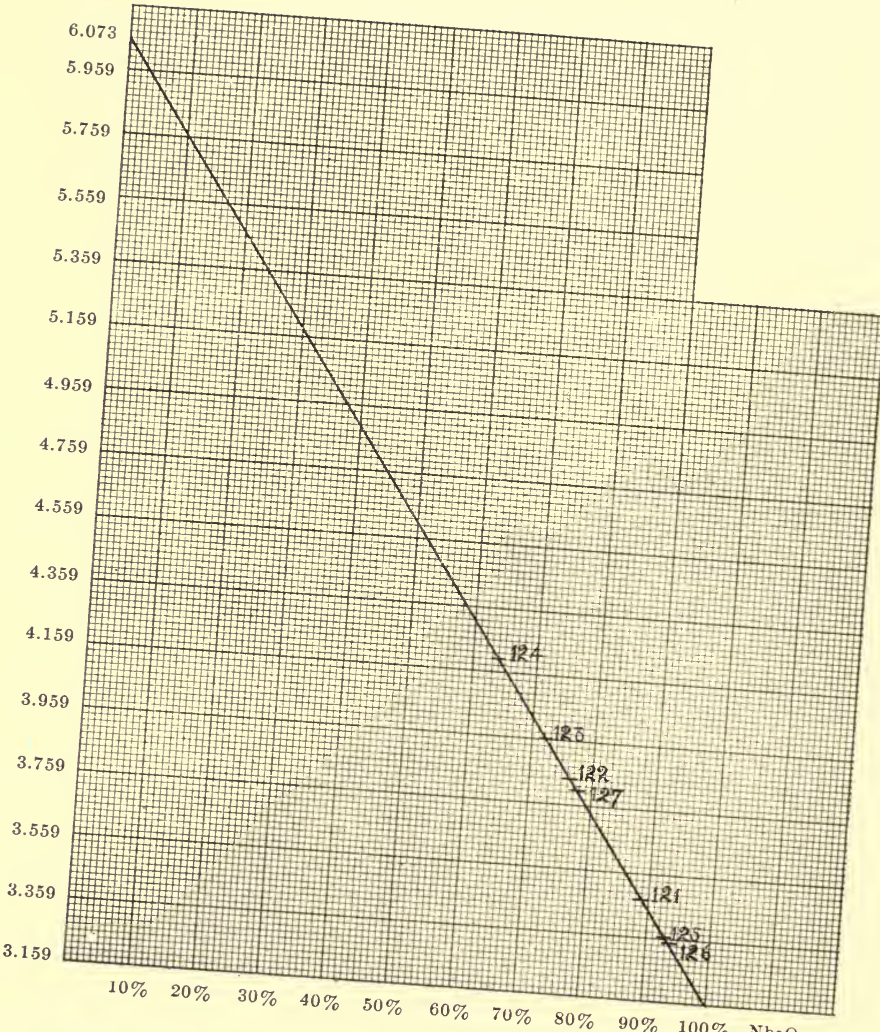
The agreement is not as satisfactory as in the case of the niobium, but those marked A, B, C, D and E are taken as constant and averaged. This gives 6.073 as the value of tantalum pentoxide under these conditions. This value, with that of niobium pentoxide, 3.159, was used to plot a curve. (Curve I.)

Mixtures of the two pure oxides were now made, fused with potassium bisulphate, and the oxides obtained in the usual manner. Determinations were made on these mixtures in the same way as those above until the specific gravity became more or less constant.

No.	Weight Ta_2O_5.	Weight Nb_2O_5.	Per Cent. Ta_2O_5	Per Cent. Nb_2O_5	Weight Oxide.	Time of Heating.	Gravity Referred to $CHCl_3$	Nb_2O_5 from Curve.	Error.
121	0.1224	1.0826	10.15	89.85	1.2044	30 mins.	3.575		
					1.1892	30 " more.	3.565		
					1.1732	30 " "	3.517		
					1.1246	40 " "	3.481	89.00%	0.85%
122	0.2417	0.9617	20.09	79.91	1.0515	40 mins.	3.836	76.60%	3.31%
					1.0289	20 " more.	3.844		
123	0.3614	0.8416	30.05	69.95	1.1952	30 mins.	3.962	72.50%	2.55%
124	0.4813	0.7211	40.03	59.97	1.1518	30 mins.	4.209	64.20%	4.23%
					1.1293	30 " more.	4.201		
125	0.1218	1.0808	10.12	89.88	1.1348	20 mins.	3.431		
					1.1054	30 " more.	3.367	92.80%	2.92%
126	0.1219	1.0813	10.14	89.86	1.2032	80 mins.	3.343		
					1.1845	20 " more.	3.369		
					1.1757	40 " "	3.352	93.40%	3.54%
127	0.4059	0.7962	33.77	66.23	1.2021	80 mins.	3.794		
					1.1868	20 " more.	3.807	77.60%	11.37%

(121) Before these determinations were made, the mixture of oxides was heated for one hour at a full red heat.

(122) This mixture was prepared as in (121) with the exception that after heating for one and a half hours the oxides were ground and boiled with water, to remove any possible soluble impurity. On filtering, the powder was too fine and ran through the filter to some extent. It was washed with alcohol, dried and taken from the paper. Heat was applied for twenty min-



CURVE I

One Division = 0.02 Specific Gravity or 1.0 per cent.

utes, the oxides cooled and placed in a desiccator for four hours, heated again for twenty minutes, and the first determination made.

(123) This mixture was treated as before until the oxides were again obtained. These were then heated for one hour at a full red heat, cooled in a desiccator, again heated for twenty minutes and the determination made.

(124) In this case, after obtaining the hydroxides the first time, they were dissolved in hydrofluoric acid, filtered, the solution taken down to fumes with sulphuric acid and rehydrolyzed. The oxides were dried, heated one and a half hours, pulverized, heated again for thirty minutes and the gravity taken.

(125) After the hydroxides had been obtained by fusion with potassium bisulphate and hydrolyzing they were dissolved in hydrofluoric acid, filtered, taken down to fumes with sulphuric acid, again hydrolyzed, washed and dried as usual. Heat was applied for one and a half hours, the oxides powdered and heated again for 20 minutes and the first determination made.

(126) In this case the oxides were merely mixed and not fused with potassium bisulphate. This should have given results according to the curve, being a simple mixture. Before the first determination they were heated for one hour and twenty minutes.

(127) This experiment was of somewhat the same character as 126, but in this case the oxides were heated separately for one hour and twenty minutes, weighed, mixed, weighed again and the specific gravity taken. In the second determination the two, mixed, were heated for twenty minutes and the specific gravity taken.

These results are unreliable from a quantitative point of view and could not be depended upon for the estimation of Nb_2O_5 and Ta_2O_5 in mixtures.

In order to determine if any change in weight took place on ignition of the oxides, quantities of each were taken, ignited one hour and weighed. They were then ignited one hour longer (Chaddock burner) and the loss in weight determined. 1.0026 grams Nb_2O_5 lost 0.0028 gram and 1.0011 grams Ta_2O_5 lost 0.0012 gram. The crucible itself showed no loss in weight.

Similarly, 4.0357 grams Ta_2O_5, which had been ignited with the blast lamp for fifteen minutes, lost 0.0010 gram on blasting for twenty-five minutes longer, and 5.0083 grams Nb_2O_5 lost 0.0045 gram on blasting for twenty-five minutes.

Part III

It was next decided to try the effect of the blast lamp on the gravity of the pure oxides, in order to establish a new basis for a curve to use with a series of mixtures, hoping by this means to obtain constant results.

Determinations were made on two portions of niobium pentoxide, blasting each time, until the gravity became practically constant.

No.	Weight Oxide.	Time of Heating.	Gravity Referred to $CHCl_3$.	
128	1.4951	20 mins.	3.170	
129	1.4752	20 " more.	3.230	
130	1.4646	20 " "	3.227	
131	1.4545	20 " "	3.262	A
132	1.4479	20 " "	3.262	A
133	1.4396	20 " "	3.268	A
134	1.4357	20 " "	3.283	A
135	1.4270	20 " "	3.262	A
136	1.4273	20 " "	3.280	A
137	1.4945	20 mins.	3.228	B
138	1.4848	20 " more.	3.255	B
139	1.4715	20 " "	3.255	B
140	1.4629	20 " "	3.263	

The average of those marked A and B is 3.265.

Determinations were made in the same manner on tantalum pentoxide and gave the following results:

No.	Weight Oxide.	Time of Heating.	Gravity Referred to CHCl .	
141	1.4528	20 mins.	6.206	A
142	1.4309	20 " more.	6.189	A
143	1.4211	20 " "	6.212	A
144	1.4122	20 " "	6.226	A
145	1.4064	20 " "	6.236	A
146	1.3935	20 " "	6.204	A
147	1.3909	20 " "	6.195	A

No.	Weight Oxide.	Time of Heating.	Gravity Referred to $CHCl_3$.
148	1.4971	20 mins.	6.183
149	1.4735	20 " more.	6.155
150	1.4695	20 " "	6.166
151	1.4622	20 " "	6.196 ⎫
152	1.4562	20 " "	6.194 ⎪
153	1.4504	20 " "	6.193 ⎬ B
154	1.4471	20 " "	6.218 ⎪
155	1.4404	20 " "	6.203 ⎭

Those marked A and B were averaged and gave 6.201. The values just obtained for tantalum and niobium oxides were used in plotting Curve II.

A series of mixtures was now made, nine in all, from 10 per cent. to 90 per cent. tantalum. These were heated with the full heat of the Chaddock burner until a practically constant gravity was obtained, then to the same mixture the blast was applied for definite periods until another constant value was reached. The first part of each group represents the determinations with the lower heat and the second part the results obtained by blasting.

No.	Weight.		Per Cent.		Weight Oxide.	Time of Heating.	Gravity Referred to $CHCl_3$	Average.
	Ta_2O_5	Nb_2O_5	Ta_2O_5	Nb_2O_5				
156	0.1228	1.0812	10.20	89.80	1.1637	90 mins.	3.500	
					1.1083	30 " more.	3.467	
					1.0942	40 " "	3.304	
					1.0825	110 " "	3.240	
					1.0677	20 " "	3.220	
					1.0725	30 " "	3.225	
				Blast				
					1.0715	15 " "	3.356	
					1.0699	30 " "	3.315 ⎫	3.316
					1.0562	15 " "	3.317 ⎭	
157	0.2415	1.0812	20.06	79.94	1.1497	90 mins.	3.890	
					1.1286	60 " more.	3.758	
					1.1192	20 " "	3.699	
					1.1029	60 " "	3.523	
					1.0935	30 " "	3.516	

No.	Weight. Ta_2O_5	Weight. Nb_2O_5	Per Cent. Ta_2O_5	Per Cent. Nb_2O_5	Weight Oxide.	Time of Heating.	Gravity Referred to $CHCl_3$	Average.
					1.0995	60 " "	3.488	
					1.0858	30 " "	3.664	
					1.0726	40 " "	3.448	
					1.0410	20 " "	3.418	
					0.0454	20 " "	3.453	
					1.0451	30 " "	3.432	
					1.0487	30 " "	3.432	
				Blast				
					1.0480	15 " "	3.414	
					1.0487	15 " "	3.438	
					1.0459	15 " "	3.464	
					0.0447	15 " "	3.488	
					1.0377	15 " "	3.497	
					1.0367	15 " "	3.481	3.484
					1.0257	15 " "	3.487	
158	0.3627	0.8420	30.10	69.90	1.1540	120 mins.	4.157	
					1.1396	40 " more.	4.200	
					1.1330	50 " "	4.177	
					1.1231	20 " "	4.182	
					1.1217	20 " "	4.154	
					1.1117	20 " "	4.184	
					1.1028	20 " "	4.186	
				Blast				
					1.0931	15 " "	3.378	
					1.0849	15 " "	3.648	
					1.0747	15 " "	3.656	
					1.0696	15 " "	3.693	3.686
					1.0682	15 " "	3.680	
159	0.4816	0.7209	40.05	59.95	1.1513	90 mins.	4.440	
					1.1303	20 " more.	4.422	
					1.1231	60 " "	4.420	
				Blast				
					1.1103	15 " "	4.017	
					1.0961	15 " "	3.904	
					1.0852	15 " "	3.919	3.908
					1.0808	15 " "	3.901	

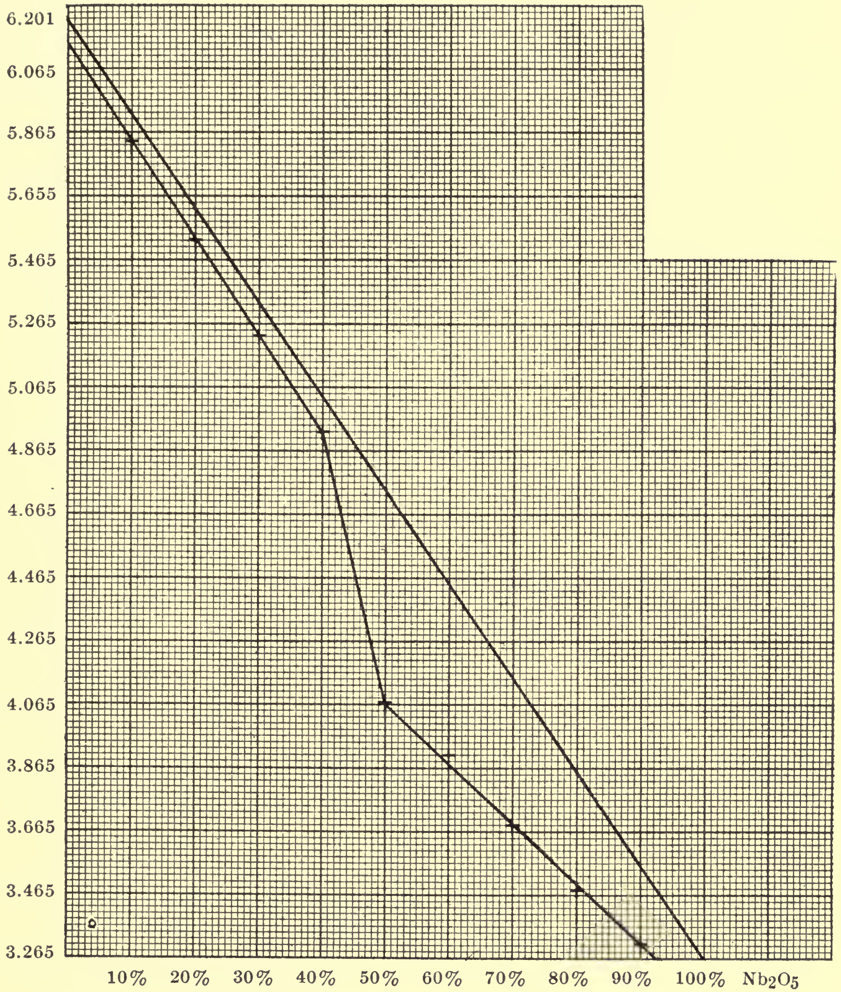
No.	Weight.		Per Cent.		Weight Oxide.	Time of Heating.			Gravity Referred to $CHCl_3$	age.
	Ta_2O_5	Nb_2O_5	T_2aO_5	Nb_2O_5						
160	0.6016	0.6015	50.02	49.98	1.1404	120 mins.			4.583	
					1.1182	30	"	more.	4.642	
					1.1017	30	"	"	4.642	
					1.0910	20	"	"	4.644	
				Blast						
					1.0884	15	"	"	4.366	
					1.0875	15	"	"	4.308	
					1.0881	15	"	"	4.282	
					1.0835	15	"	"	4.148	
					1.0781	15	"	"	4.169	
					1.0792	15	"	"	4.163	
					1.0780	15	"	"	4.142	
					1.0736	15	"	"	4.080	
					1.0721	15	"	"	4.074	4.074
					1.0715	15	"	"	4.074	
161	0.7210	0.4810	59.98	40.02	1.1592	120 mins.			4.786	
					1.1414	20	"	more.	4.857	
					1.1293	20	"	"	4.878	
					1.1129	20	"	"	4.868	
				Blast						
					1.1136	15	"	"	4.848	
					1.1146	15	"	"	4.903	
					1.1090	20	"	"	4.926	
					1.1006	15	"	"	4.926	4.925
					1.0988	15	"	"	4.916	
					1.0947	15	"	"	4.931	
162	0.8411	0.3616	69.94	30.06	1.1323	90 mins.			5.123	
					1.1163	20	"	more.	5.189	
					1.1055	20	"	"	5.202	
					1.0992	30	"	"	5.194	
					1.0895	60	"	"	5.271	
					1.0821	30	"	"	5.253	
					1.0781	20	"	"	5.266	
				Blast						
					1.0704	15	"	"	5.221	
					1.0697	15	"	"	5.223	5.227
					1.0637	15	"	"	5.237	

No.	Weight.		Per Cent.		Weight Oxide.	Time of Heating.			Gravity Referred to $CHCl_3$	Average.
	Ta_2O_5	Nb_2O_5	Ta_2O_5	Nb_2O_5						
163	0.9612	0.2410	79.95	20.05	1.1102	90 mins.			5.178	
					1.0883	20	"	more.	5.301	
					1.0814	20	"	"	5.337	
					1.0796	50	"	"	5.363	
					1.0681	80	"	"	5.460	
					1.0588	40	"	"	5.443	
					1.0573	30	"	"	5.469	
				Blast						
					1.0484	15	"	"	5.454	
					1.0452	15	"	"	5.486	
					1.0416	15	"	"	5.522	
					1.0354	30	"	"	5.475	
					1.0342	15	"	"	5.530	5.530
164	1.0823	0.1229	89.80	10.20	1.1360	120 mins.			5.601	
					1.1126	30	"	more.	5.816	
					1.1015	20	"	"	5.773	
					1.0967	30	"	"	5.808	
					1.0857	30	"	"	5.774	
				Blast						
					1.0803	15	"	"	5.827	
					1.0819	15	"	"	5.845	
					1.0788	15	"	"	5.838	5.843
					1.0709	15	"	"	5.845	

Although the values obtained on these mixtures do not fall on the curve obtained from the pure oxides, nevertheless, they are quite regular, the greatest variation among themselves being about one per cent. It is interesting to note the sudden break in the curve between the 40 and 50 per cent. mixtures. Whether or not this break is due to the formation of a compound of the two oxides the author was unable to determine.

In view of the fact that the curve obtained on these mixed oxides was so regular, it was hoped that satisfactory results might be obtained on the analysis of a sample of columbite. The mineral used was the same "Columbite A" analyzed volumetrically by Metzger and Taylor,[1] which gave an average value

[1] To be published soon.



CURVE II

One Division = 0.02 Specific Gravity or 1.0 per cent.

of 54.21 per cent. niobium pentoxide and 22.75 per cent. tantalum pentoxide, which means that the mixed oxides would be composed of 70.43 per cent. niobium pentoxide and 29.57 per cent. tantalum pentoxide.

Three different portions were treated, as follows: The ore was fused with potassium bisulphate and the melt boiled with about one liter of water. The impure hydroxides so obtained were filtered, washed with boiling water until the filtrate gave only a faint test for sulphuric acid, treated on the filter with yellow ammonium sulphide, washed again and treated with hot dilute sulphuric acid. The washed hydroxides were dissolved through the filter paper with hydrofluoric acid, the solution taken down to fumes with sulphuric acid, rehydrolyzed, boiled with water and washed by decantation twice, the last wash water being made alkaline with ammonium hydroxide. The hydroxides were then filtered, dried, blasted for definite periods and the gravity taken.

No.	Amount Ore Taken.	Weight of Oxides.	Per Cent. of Oxides.	Weight Oxides.	Time of Heating.	Gravity Referred to $CHCl_3$.	Average.
165	2.0023	1.5458	77.25	1.5266	30 mins.	3.487	
				1.5011	20 " more.	3.514	
				1.4929	20 " "	3.560	
				1.4857	20 " "	3.578	
				1.4764	20 " "	3.587	
				1.4692	40 " "	3.592	
				1.4656	20 " "	3.610	
				1.4620	20 " "	3.618	
				1.4586	25 " "	3.616	3.612
				1.4568	20 " "	3.600	
				1.4502	20 " "	3.618	
166	2.0019	1.5446	77.15	1.5279	20 mins.	3.479	
				1.5159	40 " more.	3.519	
				1.5052	20 " "	3.553	
				1.5049	20 " "	3.574	
				1.4981	20 " "	3.599	
				1.4927	20 " "	3.599	
				1.4938	25 " "	3.617	
				1.4910	20 " "	3.612	3.616
				1.4872	20 " "	3.620	

No.	Amount Ore Taken.	Weight of Oxides.	Per Cent. of Oxides.	Weight Oxides.	Time of Heating.	Gravity Referred to CHCl.	Average.
167	2.0000	1.5382	76.91	1.5271	20 mins.	3.282	
				1.5081	20 " more.	3.462	
				1.4985	20 " "	3.543	
				1.4908	75 " "	3.572	
				1.4918	20 " "	3.580	3.577
				1.4840	40 " "	3.578	

(165) According to the curve, the value 3.612 gives 74.4 per cent. Nb_2O_5, and calculating from this, the ore contains 57.43 per cent. Nb_2O_5, an error of 3.22 per cent.

(166) This value, 3.616, is very close to that of 165 and the per cent. of Nb_2O_5 cannot be read closer than 74.4 per cent. on the curve. This gives 57.47 per cent. Nb_2O_5 in the ore, an error of 3.24 per cent.

(167) The value 3.577 gives 76.4 per cent. as the amount of Nb_2O_5 in the mixture. This is equal to 58.75 per cent. Nb_2O_5 in the ore, an error of 4.54 per cent.

Conclusions.

The mixtures of oxides, as prepared by fusion with potassium bisulphate, hydrolysis, etc., do not follow the straight line of the curve.

The specific gravity of the oxides varies slightly with the method of preparation and greatly with the length of time and intensity of the heating.

As a method for the determination of the percentages of niobium and tantalum in a mixture of the two oxides, it can only be relied upon to an accuracy of about five per cent.

In general, the specific gravity of niobium pentoxide decreases with increase in temperature and length of time of heating, while that of tantalum pentoxide increases under the same conditions.

The average values of the specific gravity of niobium and tantalum pentoxides under the different conditions tried are:

	Referred to water.	Referred to chloroform.
NIOBIUM PENTOXIDE.		
At a low red heat................	4.949	.....
At a bright red heat.............	4.828	3.159
At temperature of blast..........	.....	3.265
TANTALUM PENTOXIDE.		
At a low red heat................	7.872	.....
At a bright red heat.............	8.328	6.073
At temperature of blast..........	.....	6.201